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SPECIFICATION

BE IT KNOWN THAT WE, NORIKO YAGI and KIYOSHIGE MURAOKA, all residing at c/o Sumitomo Rubber Industries, Ltd., 6-9, 3-chome, Wakinohama-cho, Chuo-ku, Kobe-shi, Hyogo-ken, Japan, subjects of Japan, have invented certain new and useful improvements in

RUBBER COMPOSITION FOR TYRE TREADS AND PNEUMATIC TYRE HAVING TREAD THEREOF

of which the following is a specification:-

RUBBER COMPOSITION FOR TYRE TREADS AND
PNEUMATIC TYRE HAVING TREAD THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to a rubber composition for tyre
treads and a pneumatic tyre having a tread made of the rubber
composition, and particularly relates to a rubber composition for tyre
5 treads significantly improving tyres in grip performance on wet road with
remaining low fuel consumption of automobiles and a pneumatic tyre
having a tread made of the rubber composition.

In recent years, tyres for automobiles require various
performances such as the controllability in driving, abrasion resistance,
10 and the comfortableness in riding as well as the low fuel consumption,
and are improved variously in these performances. Examples of
methods improving the performances, such as the performance in
braking and driving on wet road at high driving speed, and the
controllability in driving, include increasing the grip force on road
15 surface, increasing the cornering performance by increasing the block
stiffness of tyre tread pattern to inhibit the tyre from block deformation
at cornering, and inhibiting hydroplaning from arising by inhibiting
groove parts on tyre tread from deforming to lead smooth draining.
Recently, to satisfy these requirements, tyres having an increased grip
20 performance on wet road surface are provided by using rubber
compositions obtained by mixing silica with SBR of high styrene unit
contents for the treads thereof.

However, the rubber compositions for tyre treads mentioned
above provide an increased grip force at low temperature range of at

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most 15°C of road surface, but does not provide a sufficient grip force on wet or semi-wet road surface. Rubber compositions comprising silica decrease in stiffness and decreases significantly in grip force with the repetition of driving. Rubber compositions comprising silica have problems such as increased Mooney viscosity and decreased processability, for example, in extruding if the silica disperses insufficiently in the rubber compositions.

Various proposals are made traditionally to solve these problems mentioned above. As rubber compositions effective to improve grip performance of tyres, for example, Japanese unexamined patent publication No. 133375/1995, and No. 311245/1996 disclose rubber compositions obtained by mixing calcined clay with diene rubbers, and Japanese unexamined patent publication No. 3373/1996 discloses rubber compositions obtained by mixing vulcanized rubber powders comprising diene rubbers and kaolinite with specific kinds of diene rubbers. As rubber compositions showing same effects, Japanese unexamined patent publication No. 59893/1996 discloses rubber compositions obtained by mixing specific kinds of inorganic powders and carbon black with SBR comprising specific amount of styrene units, and Japanese unexamined patent publication No. 149954/1995 and No. 31250/1997 disclose rubber compositions obtained by mixing kaolinite base clay with diene rubbers having a specific ratio of 1,2-bond in the butadiene units part.

However, no rubber composition provided shows an excellent wet grip performance with a remained low heat build up characteristic and without decreased processability and decreased abrasion resistance.

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SUMMARY OF THE INVENTION

One of the objects of the present invention is to provide a rubber composition for tyre treads that significantly improves tyres in wet skid performance without decreased abrasion resistance and increased rolling resistance and to provide an improved pneumatic tyre.

The present invention relates to a rubber composition for tyre treads, which comprises (A) 100 parts by weight of a diene rubber comprising at least 35 % by weight of a styrene-butadiene rubber, (B) 5 to 50 parts by weight of clay, (C) at least 5 parts by weight of silica having a nitrogen absorption specific surface area of 100 to 300 m²/g and (D) at least 1 parts by weight of carbon black having a nitrogen absorption specific surface area of 70 to 300 m²/g, which has a total amount of (B) clay and (C) silica of at least 30 parts by weight and a total amount of (B) clay, (C) silica and (D) carbon black of at most 100 parts by weight.

The present invention relates to the above mentioned rubber composition for tyre treads, wherein (B) clay has an average particle size of at largest 10 µm.

The present invention relates to the above mentioned rubber composition for tyre treads, which comprises (E) a silane coupling agent.

The present invention relates to a pneumatic tyre which has a tread made of the above mentioned rubber compositions.

DETAILED DESCRIPTION

A rubber composition of the present invention comprises (A) a diene rubber as a rubber component. Examples of the diene rubber used in the present invention include natural rubber and synthetic diene rubbers such as a styrene-butadiene rubber (SBR), a

polybutadiene rubber (BR), a polyisoprene rubber (IR), an ethylene-propylene-diene rubber (EPDM), a chloroprene rubber (CR), an acrylonitrile-butadiene rubber (NBR), and a butyl rubber (IIR).

5 The diene rubber necessarily comprises at least 35 % by weight of SBR, but can comprise at least two kinds of diene rubbers. The diene rubber comprising less than 35 % by weight of SBR shows decreased processability at tyre production, and cannot lead the low fuel consumption to compatible with the wet grip performance. The diene rubber comprises preferably 35 to 100 % by weight, and more preferably 10 40 to 100 % by weight of SBR from the viewpoint of processability.

The SBR rubber comprises preferably 15 to 60 % by weight of styrene units. The SBR comprising less than 15 % by weight of styrene units does not provide the desirable grip performance at low and high temperature range. The SBR comprising more than 60 % by weight of 15 styrene units does not provide the desirable grip performance because shows an increased excessive block stiffness.

SBR to be used can be produced by any polymerization process such as emulsion polymerization or solution polymerization.

A rubber composition of the present invention comprises clay. 20 Clay preferably used has an average particle size of at most 10 μm . Clay having an average particle size of more than 10 μm does not show sufficient reinforcing effect and tends to decrease the abrasion resistance. Clay having too small average particle size agglomerates easily, is difficult to disperse in rubber components, and does not 25 provide a rubber composition having desirable performance in some cases. Clay to be used has an average particle size of preferably 0.1 to 10 μm , and more preferably 0.5 to 10 μm from the viewpoint of, for

example, the balance among reinforcing performance, the wet grip performance, the low fuel consumption performance and the like.

5 A rubber composition of the present invention comprises clay of 5 to 50 parts by weight, preferably 10 to 40 parts by weight. Clay of less than 5 parts by weight provides low improvement effect in the wet grip performance. Clay of more than 50 parts by weight decreases the abrasion resistance.

10 A rubber composition of the present invention comprises silica. Silica is used to supplement the reinforcing performance with clay and to decrease the rolling resistance. Silica to be used has a nitrogen absorption specific surface area (N_2SA) of 100 to 300 m^2/g , and preferably 130 to 280 m^2/g . Silica having less than 100 m^2/g of N_2SA shows a low reinforcing effect. Silica having more than 300 m^2/g of N_2SA shows a decreased dispersibility and increases the heat build up
15 characteristic.

Examples of silica to be used include silica generally used for reinforcing rubbers without limitation, for example, silica from a dry process, silica from a wet process.

20 A rubber composition of the present invention comprises silica of at least 5 parts by weight, and preferably 5 to 85 parts by weight based on 100 parts by weight of the rubber component. Silica of Less than 5 parts by weight does not show sufficient reinforcing effect and sufficient effect decreasing the rolling resistance. Silica of more than 85 parts by weight is not preferable because increases the heat build up
25 characteristic and decreases the processability.

A rubber composition of the present invention comprises carbon black. Carbon black to be used has a nitrogen absorption

specific surface area (N_2SA) of 70 to 300 m^2/g , and preferably 90 to 250 m^2/g . Carbon black having less than 70 m^2/g of N_2SA is difficult to provide the sufficient abrasion resistance because of insufficient reinforcing performance. Carbon black having 300 m^2/g of N_2SA shows
5 a low dispersibility and increases the heat build up characteristic. Examples of carbon black are not limited and include HAF, ISAF, and SAF.

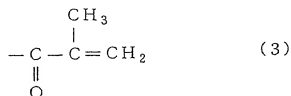
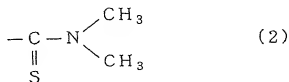
A rubber composition of the present invention comprises carbon black of at least 1 part by weight, preferably 1 to 70 parts by
10 weight, and more preferably 5 to 65 parts by weight based on the rubber component. Carbon black of less than 1 part by weight shows a low reinforcing performance and decreases the abrasion resistance. Carbon black of more than 70 parts by weight shows a low dispersibility and does not provide the desirable performances.

15 A rubber composition of the present invention comprises (B) clay and (C) silica in a total amount of 30 to 99 parts by weight based on 100 parts by weight of the rubber component. The total amount of less than 30 parts by weight does not show sufficient reinforcing effect. The total amount of more than 99 parts by weight shows decreased
20 dispersibility and increases the heat build up characteristic. The total amount is preferably 40 to 79 parts by weight from the viewpoints of effects by the addition and the properties.

A rubber composition of the present invention comprises (B) clay, (C) silica and (D) carbon black in a total amount of 31 to 100 parts
25 by weight based on 100 parts by weight of the rubber component. The total amount of less than 31 parts by weight does not show sufficient reinforcing effect. The total amount of more than 100 parts by weight

shows decreased dispersibility and increases the heat build up characteristic. The total amount is preferably 41 to 80 parts by weight from the viewpoints of effects by the addition, the properties and the like.

A rubber composition of the present invention can comprise
 5 a silane-coupling agent strengthening the bond force between the fillers and the rubber component to show increased abrasion resistance. A silane-coupling agent preferably used is represented by the formula: $Y_3-Si-C_nH_{2n}A$. In the formula, Y is an alkyl or alkoxy group having 1 to 4 carbon atoms, or chlorine atom. Each of three Y can be same or
 10 different each other. The subscript n is an integer of 1 to 6. A is a group selected from the group consisting of $-S_mC_nH_{2n}Si-Y_3$ group, nitroso group, mercapt group, amino group, epoxy group, vinyl group, chlorine atom, imido group and $-S_mZ$ group, wherein the subscript m is an integer of 1 to 6, the subscript n and Y are defined above, and Z is the
 15 following formulae (1), (2) or (3).



Examples of the silane-coupling agent include bis(3-triethoxysililpropyl)tetrasulfide, bis(2-triethoxysililethyl)tetrasulfide, bis(3-trimethoxysililpropyl) tetrasulfide, bis(2-trimethoxysililethyl)tetrasulfide,

- 5 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 2-mercaptoethyltrimethoxysilane, 2-mercaptoethyltriethoxysilane, 3-nitropropyltrimethoxysilane, 3-nitropropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane, 2-chloroethyltrimethoxysilane, 2-chloroethyltriethoxysilane,
- 10 3-trimethoxysililpropyl-N, N-dimethylthiocarbamoyltetrasulfide, 3-triethoxysililpropyl-N, N-dimethylthiocarbamoyltetrasulfide, 2-triethoxysililethyl-N, N-dimethylthiocarbamoyltetrasulfide, 3-trimethoxysililpropylbenzothiazoltetrasulfide, 3-triethoxysililpropylbenzothiazoltetrasulfide,
- 15 3-triethoxysililpropylmethacrylatemonosulfide, 3-trimethoxysililpropylmethacrylatemonosulfide.

Examples of the silane-coupling agent having three Y different from each other include

- bis(3-diethoxymethylsililpropyl)tetrasulfide,
- 20 3-mercaptopropyldimethoxymethylsilane, 3-nitropropyldimethoxymethylsilane 3-chloropropyldimethoxymethylsilane, dimethoxymethylsililpropyl-N, N-dimethylthiocarbamoyltetrasulfide, dimethoxymethylsililpropylbenzothiazoltetrasulfide.
 - 25 Bis(3-triethoxysililpropyl)tetrasulfide, and 3-trimethoxysililpropylbenzothiazoltetrasulfide are preferable from the viewpoint of the compatibleness between effects of adding the coupling

agents and the costs.

Silane-coupling agents can be used singly or in combination of at least two of them.

Silane-coupling agents are used preferably in an amount of 1
5 to 20 % by weight based on the total amount of clay and silica.
Silane-coupling agents of less than 1 % by weight do not show sufficient
effects. More than 20 % by weight do not provide increased coupling
effects corresponding to the increased cost and decrease the reinforcing
performance and the abrasion resistance. Silane-coupling agents are
10 used preferably in an amount of 2 to 15 % by weight from the viewpoints
of dispersion effects and coupling effects.

A rubber composition of the present invention can comprise
other components or agents used in a general rubber industry such as
softners, antioxidants, vulcanization agents, vulcanization accelerators,
15 and vulcanization accelerator assistants as well as rubber components,
clay, silica, carbon black, and silane-coupling agents.

A rubber composition for tyre treads of the present invention
is useful for materials constituting treads of pneumatic tyres, and
improves the wet grip performance significantly without decreasing the
20 abrasion resistance and the rolling resistance.

The present invention provides a rubber composition for tyre
treads providing a significantly improved wet skid performance without
decreasing the abrasion resistance and without decreasing the rolling
resistance of the tyres and an improved pneumatic tyre having a tread
25 made of the rubber composition.

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EXAMPLES

The present invention is explained in more detail based on the following Examples, but the present invention is not limited thereto.

Raw materials used in Examples and Comparative Examples

5 are shown below.

Natural rubber: RSS #3 grade

Diene rubber (SBR): SBR1502 comprising 23.5 % by weight of styrene units available from Japan Synthetic Rubber Co., Ltd.

Clay: Crown clay comprising 86 % by weight of particles having a size of
10 at largest 2 μm and 4 % by weight of particles having a size of larger than 2 μm and at largest 5 μm available from South Eastern Co., Ltd.

Silica: Ultrasil VN3 having 210 m^2/g of N_2SA available from Degussa Co., Ltd.

Carbon black: SHOWBLACK N220 having 125 m^2/g of N_2SA available
15 from Showa Cabot K. K.

Silane-coupling agent: Si69 (bis(3-triethoxysililpropyl)tetrasulfide) available from Degussa Co., Ltd.

Aromatic oil: JOMO PROCESS X140 available from Japan Energy Corporation.

20 Antioxidant: NOCRAC 6C (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) available from Ouchishinko Chemical Industrial Co., Ltd.

Stearic acid: available from NOF Corporation.

Zinc oxide: Zinc oxide No.1 available from Mitsui Mining & Smelting Co.,
25 Ltd.

Sulfur: sulfur powders available from Tsurumi Chemical Co., Ltd.

Vulcanization accelerator TBBS: Nocceller NS (N-tert-butyl-2-

benzothiazylsulfenamide) available from Ouchishinko Chemical Industrial Co., Ltd.

Vulcanization accelerator DPG: Nocceller D (N, N'-diphenylguanidine) available from Ouchishinko Chemical Industrial Co., Ltd.

5 Evaluation methods used in Examples and Comparative Examples are shown below.

(Abrasion Test)

Lambourn abrasion test was conducted by using a ranbone abrasion tester under the condition of 20°C of temperature, 20 % of slip
10 ratio, and 5 min of testing time. Volume loss of each composition was calculated and indexed according to the following equation based on Comparative Example 1 indexed 100. A high value of the index shows an excellent performance in the abrasion resistance.

$$\begin{aligned} & \text{(Lambourn abrasion index)} = \text{(Volume loss of Comp. Ex. 1)} \\ & \quad + \text{(Volume loss of each compositions)} \times 100 \\ & \text{(Rolling Resistance Index)} \end{aligned}$$

Loss tangent ($\tan \delta$) of each composition was measured by using Viscoelastic Spectrometer VES available from Iwamoto Seisakusho K.K. under the condition of 70°C of temperature, 10 % of
20 initial strain, and 2 % of dynamic strain, and indexed according to the following equation (Rolling Resistance Index). A high value of the index shows an excellent performance in the rolling resistance.

(Rolling Resistance Index)

$$= (\tan \delta \text{ of Comp. Ex. 1}) + (\tan \delta \text{ of each composition}) \times 100$$

25 (Wet Skid Test)

Skid resistance was measured by using a portable skid resistance tester available from Stanley Co., Ltd. according to ASTM

E303-83 under 25°C, and indexed according to the following equation (Wet Skid Index). A high value of the index shows an excellent performance in the wet skid performance.

$$(\text{Wet Skid Index}) = (\text{Skid resistance of each composition})$$

5

$$+ (\text{Skid resistance of Comp. Ex. 1}) \times 100$$

EXAMPLES 1 to 4 and COMPARATIVE EXAMPLES 1 to 6

Each of rubber compositions for tests was obtained by mixing the components according to the proportion shown in Table 1.

- 10 Vulcanized rubber compositions were obtained by vulcanizing the rubber compositions with pressing under 170°C for 20 min.

Results are shown in Table 1.

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TABLE 1

Raw materials (parts by weight)												
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4	Com. Ex. 5	Com. Ex. 6		
Natural Rubber	-	-	-	65	-	-	-	-	75	-		
SBR	100	100	100	35	100	100	100	100	25	100		
Clay	5	15	30	10	-	-	-	10	10	10		
Silica	30	20	20	20	60	-	30	10	10	40		
Carbon Black	25	25	25	30	-	60	30	40	40	60		
Silane-Coupling Agent	3.5	3.5	5	3	6	-	3	2	2	5		
Aromatic Oil	8	8	8	8	20	20	20	8	8	15		
Antioxidant	1	1	1	1	1	1	1	1	1	1		
Stearic Acid	2	2	2	2	2	2	2	2	2	2		
Zinc Oxid	3	3	3	3	3	3	3	3	3	3		
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5		
Vulcanization accelerator TBBS	1	1	1	1	1	1	1	1	1	1		
Vulcanization accelerator DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		
Characteristics												
Ranbone Abrasion Index	107	106	103	102	100	112	105	109	107	104		
Rolling Resistance Index	102	105	108	101	100	83	95	94	87	80		
Wet Skid Index	110	116	120	102	100	85	91	90	84	93		

Improved wet skid performances were shown without decreased abrasion resistances and decreased rolling resistances in Examples 1 to 4 wherein (B) clay, (C) silica and (D) carbon black were used in combination with defined proportions.

- 5 Insufficient wet skid performances were provided in Comparative Examples 1 to 3 wherein each of (C) silica and (D) carbon black was used singly or (C) silica and (D) carbon black were used in combination without (B) clay. Insufficient wet skid performances and rolling resistances were provided in Comparative Examples 4 and 5
- 10 wherein (B) clay, (C) silica and (D) carbon black were used in combination with a total amount of less than 30 parts by weight of (B) clay and (C) silica based on 100 parts by weight of the rubber component, and in Comparative Example 6 wherein (B) clay, (C) silica and (D) carbon black were used in a total amount of more than 100 parts by weight.

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